the one labeled I in the figure. The view shown coincides with the C_3 axis of the molecule so that the chloroform hydrogen atom lies directly behind the carbon atom shown, the C–H bond making an angle of 14 ± 3° with the C–Cl vector. Using this angle and the C–Cl contact distance of 3.65 ± 0.03 Å, together with an assumed C–H bond length of 1.07 Å, the H···Cl contact between the chloroform hydrogen atom and the axial chlorine atom of the dimer may be calculated as 2.6 Å, suggesting an appreciable degree of hydrogen-bonding interaction.[23] McGinnety, *et al.*, report similar evidence for C–H···I hydrogen bonding between methylene chloride and iodine in a recent paper.[24] Although considerable spectroscopic and calorimetric data indicate that C–H···B hydrogen bonding can occur when the carbon atom bears electronegative substituents,[25] there is little structural evidence available to support these findings. Observation of intensity or frequency changes in the infrared C–H stretching mode of the chloroform molecule which would support the presence of hydrogen bonding in the present instance is precluded by the C–H vibrations of the phenyl rings, which occur in the same region of the spectrum.

(23) (a) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, Table 1-1, p 16. Calculated and observed values for H···Cl in N–H···Cl of 3.0 and 2.4 Å, respectively, suggest that 2.6 Å for H···Cl in C–H···Cl is a reasonable value. (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman Co., San Francisco, Calif., 1960, Table 9-XXV, pp 290, 291. Extension of tabulated N–H···Cl contacts by 0.1 Å predicts C–H···Cl hydrogen-bonding contacts up to about 3.6 Å.

(24) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(25) Reference 23b, Section 6.2, pp 197–201.

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The Crystal Structure of Aluminum Tetrahydroborate–Trimethylamine at 25 and −160°

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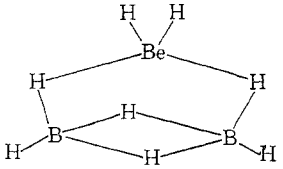
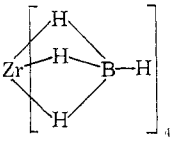
Aluminum tetrahydroborate–trimethylamine, $(CH_3)_3N{\rightarrow}Al(BH_4)_3$, forms orthorhombic crystals with unit cell parameters a = 13.02 Å, b = 7.53 Å, c = 11.33 Å, Z = 4, ρ_{calcd} = 0.781 g/cc at 25° and a = 12.88 Å, b = 7.15 Å, c = 11.40 Å, Z = 4 at −160°; the space group is Pnam at both temperatures. The room- and low-temperature structure determinations, from data collected by photographic methods, have converged to discrepancy indices of 0.103 and 0.091 based on 388 and 597 independent reflections, respectively; in the low-temperature structure, hydrogen atoms were located. In the monomeric complex, the coordination of the aluminum atom is approximately tetrahedral at room temperature, but at low temperature the coordination is asymmetric; the nitrogen atom shows near-tetrahedral coordination in both structure determinations. At room temperature the mean skeletal bond lengths (in Å) are: N–C, 1.59 (σ = 0.02); Al–N, 2.00 (σ = 0.01); Al–B, 2.19 (σ = 0.02); at low temperature these become: N–C, 1.52 (σ = 0.01); Al–N, 1.99 (σ = 0.01); Al–B, 2.24 (σ = 0.01); and the two distinct N–Al–B bond angles are 121.8° (σ = 0.4°) and 100.8° (σ = 0.3°). The relationship between the two structures is discussed in the light of disordering and exchange mechanisms and the room-temperature structure is compared with those of related molecules.

Introduction

Several metal tetrahydroborates which exhibit a high degree of covalent character (*e.g.*, $Be(BH_4)_2$, $Al(BH_4)_3$, $Zr(BH_4)_4$, etc.) are now known,[1] and it has been suggested[2] that in these compounds the metal and boron atoms are linked by bridging hydrogen atoms. However, recent structure determinations by X-ray and electron diffraction methods have indicated that the type of bridging system may vary. Thus it has been suggested that $Be(BH_4)_2$[3] and $Zr(BH_4)_4$[4] possess structures I and II, respectively, although the precise positions of the hydrogen atoms have not yet been unambiguously determined. The infrared spectra and other physical



I



II

properties of $Hf(BH_4)_4$ and $U(BH_4)_4$ are closely similar to those of $Zr(BH_4)_4$,[5] and it might therefore be inferred that they have similar structures. It would therefore be of interest to compare these structures with those of other metal tetrahydroborates.

Although $Al(BH_4)_3$ is a liquid at ambient temperatures, many of its derivatives, *e.g.*, $(CH_3)_3N{\cdot}Al(BH_4)_3$, are crystalline solids,[6] and a detailed study of this adduct by X-ray diffraction was undertaken at both 25 and −160° to determine the AlB_3 skeletal arrangement and the

(1) H. G. Heal, "Recent Studies in Boron Chemistry," Royal Institute of Chemistry Monograph, No. 1, London, 1960.

(2) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

(3) A. Almenningen, G. Gundersen, and A. Haaland, *Chem. Commun.*, 557 (1967).

(4) P. H. Bird and M. R. Churchill, *ibid.*, 403 (1967).

(5) B. D. James and M. G. H. Wallbridge, to be submitted for publication.

(6) P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 3923 (1965).

positions of the hydrogen atoms. The results of these separate investigations at different temperatures have been briefly reported previously.[7] From such results it would not be unreasonable to infer the nature of the bridge bonding system in aluminum tetrahydroborate itself.[8]

Experimental Section

The adduct $(CH_3)_3N \cdot Al(BH_4)_3$ was prepared as previously described;[6] numerous crystals were mounted under nitrogen into Lindemann glass capillaries, and several suitable for further study were selected by visual inspection and from initial X-ray photographs.

X-Ray Data (Room Temperature).—The crystals, which were colorless and of irregular shape, showed orthorhombic symmetry with unit cell parameters (together with estimated standard deviations) measured from high-angle Weissenberg data of a = 13.02 Å (σ = 0.01 Å), b = 7.53 Å (σ = 0.01 Å), c = 11.33 Å (σ = 0.02 Å), and Z = 4, corresponding to ρ_{calcd} = 0.781 g/cc; an accurate observed density was not obtained owing to the reactivity of the complex in air, but it was observed that the crystals floated in dry benzene. Systematic absences, observed from Weissenberg films for $\{0kl\}$, $k + l = 2n + 1$, $\{h0l\}$, $h = 2n + 1$, revealed the space group to be $Pna2_1$ (C_{2v}^9, no. 33) or Pnam, a nonstandard setting of Pnma (D_{2h}^{16}, no. 62); in the latter case the molecule is constrained to possess strict mirror symmetry, providing that the possibility of disorder can be excluded. The equivalent positions for space group Pnam are (x, y, z): $^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$; $^1/_2 + x$, $^1/_2 - y$, z; $-x$, $-y$, $^1/_2 + z$; x, y, $^1/_2 - z$; $^1/_2 - x$, $^1/_2 + y$, $-z$; $^1/_2 + x$, $^1/_2 - y$, $^1/_2 - z$; $-x$, $-y$, $-z$.

Three-dimensional, X-ray data were collected by Weissenberg photographic methods using unfiltered Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) and were estimated visually. Since excessive decompositon occurred after a few days, several crystals, aligned up the b and c axes, were needed to collect data of the type $\{h0l\}$ through $\{h3l\}$ and $\{hk0\}$ through $\{hk5\}$. Corrections were applied for absorption (μ = 10.0 cm^{-1}) by means of a 512-point Gaussian integration method similar to that described by Busing and Levy;[9] corrections for splitting of the Kα doublet were also applied. No systematic corrections for extinction were made and no evidence for extinction was observed during subsequent refinement. The data were scaled together by consideration of common reflections and comprised 388 independent reflections.

Structure Solution and Refinement.—A three-dimensional Patterson synthesis revealed only very approximate coordinates for the aluminum atom, but on sharpening the reflections by the method of Lipscomb, *et al.*,[10] images of the aluminum–nitrogen vector were clearly seen in the sections Z = 0 and Z = 0.5 of the sharpened Patterson synthesis. This yielded trial coordinates for the aluminum and nitrogen atoms and suggested that the molecule possessed at least approximate mirror symmetry. An observed Fourier synthesis based on structure factors phased by the aluminum and nitrogen atoms in space group Pnam showed all light atoms (excluding hydrogen atoms) in positions consistent with the space group of higher symmetry. Several cycles of block-diagonal, least-squares refinement (using a computer program written by J. S. Rollett) of atomic positional and isotropic vibrational parameters converged the conventional discrepancy index—$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$—to a value of 0.168. All atomic scattering factors were taken from the "International Tables for X-ray Crystallography," Vol. III, p 202; the function minimized during least-squares refinement was $\Sigma(|F_o| - k|F_c|)^2$, all observed reflections were given unit weights, and all unobserved data were omitted from the refinement. The gradual introduction of anisotropic thermal parameters, defined by the expression $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$, for all atoms reduced the discrepancy index to a value of 0.105. Comparison of observed and calculated structure amplitudes revealed slight errors in scaling for layers $\{h2l\}$ and $\{hk4\}$; after correction, five cycles of full-matrix, least-squares refinement (using a computer program written by N. A. Bailey) caused convergence to be reached at R = 0.103. A difference Fourier synthesis showed no evidence of localized hydrogen atoms although there was substantial, but diffuse, electron density in the region of the boron atoms reaching a maximum height of 0.30 electron/Å^3, which was equivalent to 0.18 of the height of a boron atom in the observed Fourier synthesis. All bond lengths in the following discussion are derived from atomic positions after full-matrix refinement in which contributions to the structure factors from hydrogen atoms were excluded.

Tables I and II list the atomic positions and anisotropic vibrations, respectively, each with their standard errors. Table III lists observed structure amplitudes and calculated structure factors on the scale of electron units.

TABLE I
ROOM-TEMPERATURE ATOMIC FRACTIONAL COORDINATES AND ESD'S

	x	y	z
Al	0.0688 (4)	0.1349 (7)	0.2500
N	0.1676 (9)	−0.0691 (19)	0.2500
C_S	0.2803 (13)	−0.0031 (30)	0.2500
C_G	0.1528 (12)	−0.1863 (17)	0.1318 (14)
B_S	−0.0891 (17)	0.0239 (43)	0.2500
B_G	0.0981 (15)	0.2936 (23)	0.0949 (15)

Molecular Geometry.—The molecular geometry is shown in Figure 1; bond lengths and angles, together with their esd's, are listed in Table IV. The mean nitrogen–carbon bond length of 1.59 Å (rms deviation from the mean being 0.03 Å) is rather large as a consequence of the omission of the methyl group hydrogen atoms from the refinement. The two aluminum–boron distances deviate by 0.03 Å from the mean value of 2.19 Å. The aluminum–nitrogen bond is slightly larger than the sum of covalent radii (1.96 Å). All bond angles are within 3° (3σ) of the tetrahedral value of 109° 28′.

X-Ray Data (Low Temperature).—In an attempt to determine the positions of the hydrogen atoms associated with the tetrahydroborate groups, the structure solution was repeated with data recorded at a low temperature. The crystal was held at a temperature of −160° (±5°) by positioning it approximately 2 mm from the mouth of a delivery tube attached to a flask holding a constant head of boiling liquid nitrogen. Unit cell parameters were a = 12.88 Å (σ = 0.02 Å), b = 7.15 Å (σ = 0.01 Å), c = 11.40 Å (σ = 0.02 Å), and Z = 4. Systematic absences were unchanged from those in the room-temperature structure; data, collected and processed in the same way as that obtained at room temperature, comprised 597 independent reflections.

Comparison of atomic coordinates derived from the room-temperature structure with a three-dimensional sharpened Patterson synthesis based on the low-temperature data yielded initial coordinates for all atoms except hydrogens. Five cycles of block-diagonal, least-squares refinement of atomic positional and isotropic vibrational parameters reduced the discrepancy index to a value of 0.185. A difference Fourier synthesis clearly showed all of the hydrogen atoms in positions consistent with the higher symmetry space group, together with clear indications of anisotropic thermal motion of the heavy atoms. Least-squares refinement of positional and anisotropic vibrational parameters for the six unique heavy atoms reduced the discrep-

(7) (a) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Commun.*, 438 (1965); (b) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 286 (1966).

(8) Since this paper was submitted the structure of aluminum tetrahyroborate has been determined from electron diffraction measurements: A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **22**, 328 (1968). The aluminum atom is bonded to the boron atoms by two hydrogen bridging atoms and molecular symmetry is either D_{3h} or slightly deformed into D_3.

(9) W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).

(10) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *ibid.*, **14**, 598 (1961).

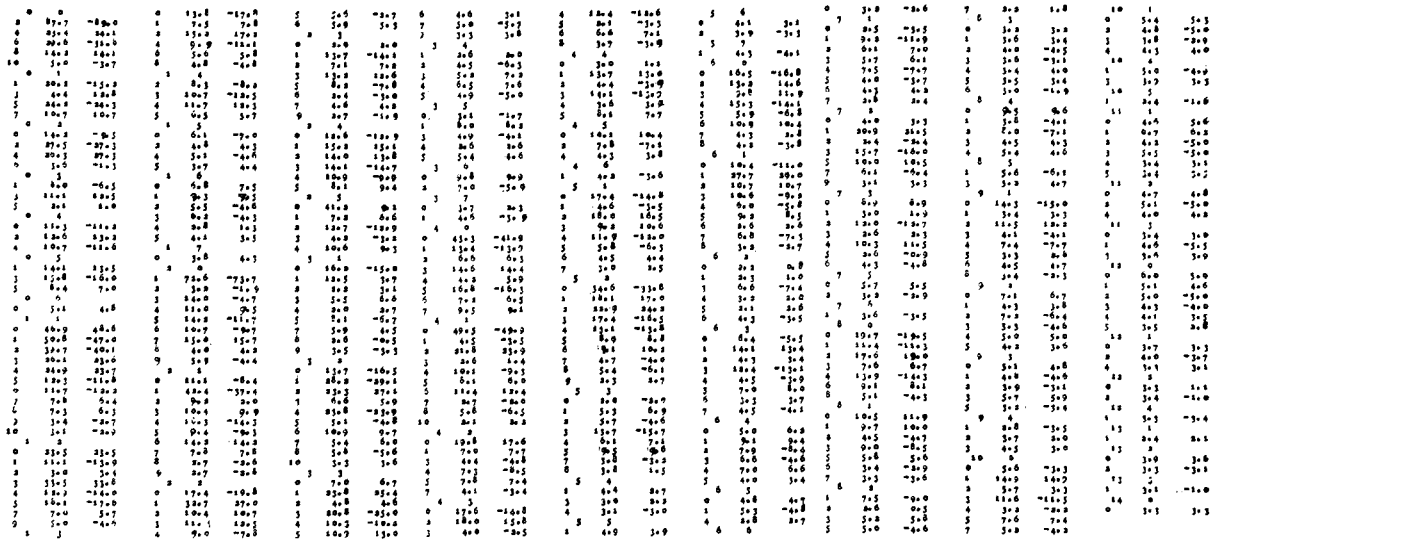
TABLE II

ROOM-TEMPERATURE ATOMIC ANISOTROPIC THERMAL VIBRATIONS AND ESD'S

	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Al	0.0096 (3)	0.0314 (12)	0.0183 (6)	0	0	−0.001 (1)
N	0.0083 (9)	0.0413 (43)	0.0289 (24)	0	0	0.005 (3)
C_S	0.0092 (13)	0.0625 (72)	0.0470 (45)	0	0	−0.007 (6)
C_G	0.0246 (18)	0.0453 (46)	0.0320 (24)	−0.037 (6)	0.001 (4)	0.017 (4)
B_S	0.0095 (16)	0.0829 (112)	0.0402 (50)	0	0	−0.002 (8)
B_G	0.0260 (22)	0.0484 (54)	0.0224 (22)	0.018 (6)	−0.002 (4)	−0.020 (6)

TABLE III

ROOM-TEMPERATURE OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS



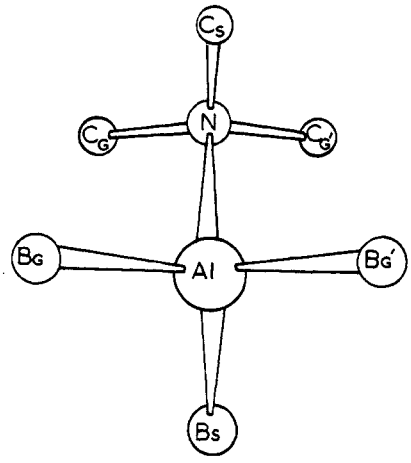


Figure 1.—Room-temperature molecular geometry.

TABLE IV

ROOM-TEMPERATURE MOLECULAR GEOMETRY AND ESD'S

	Length, Å	Esd, Å
Al–N	2.004	0.013
Al–B_S	2.218	0.023
Al–B_G	2.159	0.016
N–C_S	1.549	0.020
N–C_G	1.615	0.015
	Angle, deg	**esd, deg**
N–Al–B_S	107.8	0.9
N–Al–B_G	108.1	0.5
B_S–Al–B_G	111.9	0.6
B_G–Al–B_G'	108.9	0.6
Al–N–C_S	111.3	1.0
Al–N–C_G	110.0	0.7
C_S–N–C_G	106.8	0.8
C_G–N–C_G'	112.0	1.0

ancy index to 0.115, the contributions due to the hydrogen atoms being included in the structure factor calculations; further refinement of hydrogen positional parameters reduced R to 0.107. Comparison of observed and calculated structure amplitudes indicated slight errors in the scaling of two layers of data, $\{h1l\}$ and $\{hk5\}$, which were corrected. Full-matrix, least-squares refinement of positional parameters for all atoms, anisotropic vibrational parameters for the six heavy atoms, and isotropic vibrational parameters for the hydrogen atoms reduced R to 0.091 in five cycles. A total difference Fourier synthesis showed no peak with height greater than 0.44 electron/Å^3 (approximately 0.08 of the height of a boron atom in an observed synthesis).

Tables V and VI list the atomic positions and vibrations, respectively, together with their standard errors; the large standard

TABLE V

LOW-TEMPERATURE ATOMIC FRACTIONAL COORDINATES AND ESD'S

	x	y	z
Al	0.0662 (2)	0.1135 (3)	0.2500
N	0.1526 (5)	−0.1171 (10)	0.2500
C_S	0.2697 (7)	−0.0690 (15)	0.2500
C_G	0.1336 (6)	−0.2340 (10)	0.1422 (9)
B_S	−0.1089 (9)	0.1014 (17)	0.2500
B_G	0.1045 (8)	0.2306 (13)	0.0742 (10)
$H_S(1)$	−0.049 (6)	−0.074 (10)	0.250
$H_S(2)$	−0.067 (10)	0.245 (18)	0.250
$H_S(3)$	0.324 (11)	−0.210 (22)	0.250
$H_G(1)$	−0,148 (6)	0.107 (12)	0.160 (7)
$H_G(2)$	0.137 (5)	0.288 (9)	0.164 (6)
$H_G(3)$	0.060 (5)	0.057 (9)	0.101 (7)
$H_G(4)$	0.057 (7)	0.363 (15)	0.034 (9)
$H_G(5)$	0.170 (6)	0.150 (12)	0.006 (8)
$H_G(6)$	0.282 (5)	0.007 (11)	0.167 (7)
$H_G(7)$	0.146 (4)	−0.158 (9)	0.068 (6)
$H_G(8)$	0.055 (6)	−0.267 (11)	0.132 (7)
$H_G(9)$	0.166 (8)	−0.373 (16)	0.168 (9)

Table VI

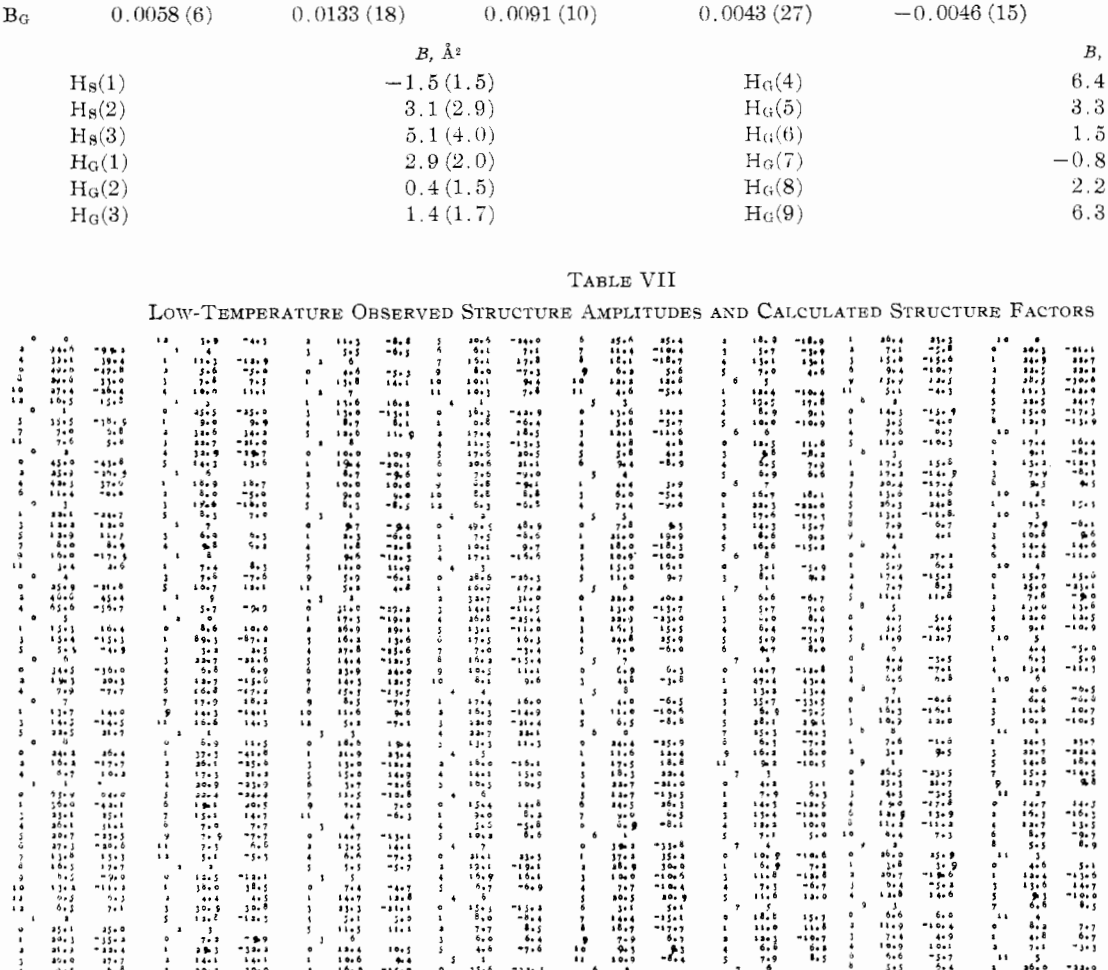
Low-Temperature Atomic Thermal Parameters and Esd's

Al	0.0019 (1)	0.0027 (4)	0.0071 (3)	0	0	0.0000 (5)
N	0.0017 (4)	0.0037 (11)	0.0073 (8)	0	0	0.0006 (12)
C_S	0.0022 (6)	0.0119 (20)	0.0113 (14)	0	0	0.0019 (16)
C_G	0.0053 (5)	0.0075 (13)	0.0088 (9)	−0.0072 (26)	−0.0001 (13)	0.0018 (12)
B_S	0.0028 (6)	0.0083 (21)	0.0142 (18)	0	0	0.0038 (21)
B_G	0.0058 (6)	0.0133 (18)	0.0091 (10)	0.0043 (27)	−0.0046 (15)	−0.0030 (18)

	B, Å²		*B*, Å²
$H_S(1)$	−1.5 (1.5)	$H_G(4)$	6.4 (2.8)
$H_S(2)$	3.1 (2.9)	$H_G(5)$	3.3 (2.1)
$H_S(3)$	5.1 (4.0)	$H_G(6)$	1.5 (1.8)
$H_G(1)$	2.9 (2.0)	$H_G(7)$	−0.8 (1.3)
$H_G(2)$	0.4 (1.5)	$H_G(8)$	2.2 (1.9)
$H_G(3)$	1.4 (1.7)	$H_G(9)$	6.3 (2.9)

Table VII

Low-Temperature Observed Structure Amplitudes and Calculated Structure Factors



errors on the hydrogen atom isotropic temperature factors show that no significance can be attached to their absolute values. Table VII lists observed structure amplitudes and calculated structure factors on the scale of electron units.

Molecular Geometry.—The molecular geometry is shown in Figure 2, and Table VIII lists bond lengths and angles together with esd's. The aluminum–nitrogen and aluminum–boron distances are substantially unchanged from the room-temperature data (maximum deviation from the mean is 2σ); the shorter mean nitrogen–carbon bond length is a consequence of the inclusion of methyl group hydrogen atoms in the least-squares refinements. The angles C_S–N–Al and C_G–N–Al indicate a significant deviation (4σ) from the tetrahedral value so as to decrease intramolecular interactions between hydrogens of the methyl and tetrahydroborate groups. The greatest difference between the room-temperature and low-temperature structures lies in the configurations of the tetrahydroborate groups. The strict tetrahedral arrangement of the boron atoms around the aluminum atom at room temperature is replaced by a distorted arrangement in which the coordination of the aluminum atom is approximately pentagonal bipyramidal, the apical positions being occupied by the nitrogen atom and one of the bridging hydrogen atoms of the "special" tetrahydroborate group ($H_S(2)$). The pentagonal plane comprises the remaining bridging hydrogen atom of the "special" tetrahydroborate group ($H_S(1)$) and the four bridging hydrogen atoms from the two (symmetry-related) "general" tetrahydroborate groups. The rms deviation of the hydrogen atoms from the plane is 0.19 Å, the apical nitrogen and hydrogen atoms both deviate by 13.5° from the true axial positions, and the aluminum atom is, within 0.5σ, coplanar with the hydrogen atoms.

Molecular Vibrations.—The rms amplitudes of vibration and the direction cosines (referred to crystal axes *a*, *b*, *c*) of the axes of the thermal ellipsoids at room temperature and low temperature are given in Table IX. Analysis of the anisotropic thermal motions of the carbon and boron atoms at room temperature shows that in all cases the direction of minimum vibration is within 34° of the nitrogen–carbon or aluminum–boron bond.

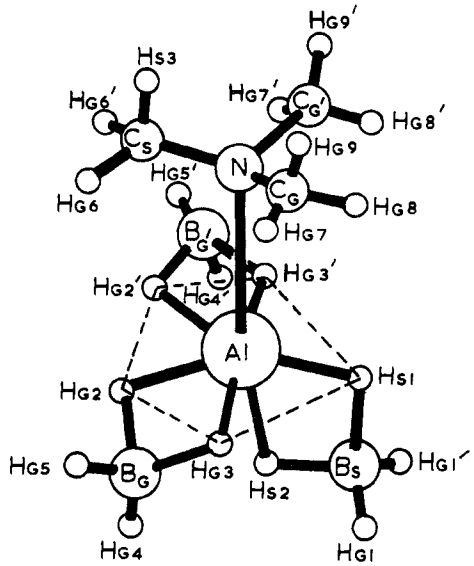


Figure 2.—Low-temperature molecular geometry.

TABLE VIII

LOW-TEMPERATURE MOLECULAR GEOMETRY AND ESD'S

	Length, Å	Esd, Å		Length, Å	Esd, Å
Al–N	1.989	0.008	B_S–$H_S(1)$	1.48	0.10
Al–B_S	2.257	0.012	B_S–$H_S(2)$	1.16	0.11
Al–B_G	2.227	0.011	B_S–$H_G(1)$	1.15	0.08
Al–$H_S(1)$	2.00	0.10	$H_S(1)$–$H_S(2)$	2.29	0.15
Al–$H_S(2)$	1.95	0.11	N–C_S	1.547	0.011
Al–$H_G(2)$	1.83	0.07	N–C_G	1.506	0.010
Al–$H_G(3)$	1.75	0.08			
			C_S–$H_S(3)$	1.22	0.18
B_G–$H_G(2)$	1.18	0.07	C_S–$H_G(6)$	1.10	0.07
B_G–$H_G(3)$	1.40	0.07	C_G–$H_G(7)$	1.02	0.07
B_G–$H_G(4)$	1.22	0.11	C_G–$H_G(8)$	1.04	0.08
B_G–$H_G(5)$	1.29	0.09	C_G–$H_G(9)$	1.12	0.10
$H_G(2)$–$H_G(3)$	2.06	0.10			

	Angle, deg	Esd, deg		Angle, deg	Esd, deg
N–Al–B_S	121.8	0.4	$H_G(2)$–B_G–$H_G(3)$	105.6	4.6
N–Al–B_G	100.8	0.3	$H_G(2)$–B_G–$H_G(4)$	103.3	6.0
B_S–Al–B_G	103.7	0.3	$H_G(2)$–B_G–$H_G(5)$	116.9	5.2
B_G–Al–B_G'	128.3	0.4	$H_G(3)$–B_G–$H_G(4)$	124.2	5.6
			$H_G(3)$–B_G–$H_G(5)$	90.3	5.0
N–Al–$H_S(2)$	152.8	3.3	$H_G(4)$–B_G–$H_G(5)$	117.0	6.6
N–Al–$H_S(1)$	81.8	2.8			
N–Al–$H_G(2)$	106.7	2.2	Al–N–C_S	111.2	0.6
N–Al–$H_G(3)$	80.5	2.3	Al–N–C_G	111.7	0.4
$H_S(2)$–Al–$H_S(1)$	71.0	4.4	C_S–N–C_G	106.3	0.4
$H_S(2)$–Al–$H_G(2)$	96.2	3.6	C_G–N–C_G'	109.4	0.6
$H_S(2)$–Al–$H_G(3)$	94.0	2.4			
$H_S(1)$–Al–$H_G(2)$	145.7	2.4	N–C_S–$H_S(3)$	111.6	7.6
$H_S(1)$–Al–$H_G(3)$	79.0	2.3	N–C_S–$H_G(6)$	104.2	3.9
$H_G(2)$–Al–$H_G(3)$	70.2	3.2	$H_S(3)$–C_S–$H_G(6)$	109.1	5.1
$H_G(2)$–Al–$H_G(2)'$	64.9	3.2	$H_G(6)$–C_S–$H_G(6)'$	118.5	5.6
$H_G(3)$–Al–$H_G(3)'$	152.6	3.2			
			N–C_G–$H_G(7)$	111.1	3.8
$H_S(1)$–B_S–$H_S(2)$	120.2	6.4	N–C_G–$H_G(8)$	111.9	4.5
$H_S(1)$–B_S–$H_G(1)$	104.9	4.3	N–C_G–$H_G(9)$	102.7	4.9
$H_S(2)$–B_S–$H_G(1)$	100.0	4.6	$H_G(7)$–C_G–$H_G(8)$	100.3	5.7
$H_G(1)$–B_S–$H_G(1)'$	128.4	5.3	$H_G(7)$–C_G–$H_G(9)$	129.6	6.1
			$H_G(8)$–C_G–$H_G(9)$	100.5	6.7

The boron atoms show large thermal motion in the nitrogen–aluminum–boron plane, approximately normal to the aluminum–boron vector. The boron atom lying in the crystallographic mirror plane shows a large amplitude of vibration perpendicular to the mirror plane indicating either static or dynamic disorder or that the space group is the one of lower symmetry; this relatively large amplitude of vibration persists at low temperature. The magnitudes and directions of these room-temperature thermal ellipsoids suggest the possibility that the asymmetric structure observed at low temperature is exchanging or is disordered at room temperature between the three tetrahydroborate groups.

Discussion

The relationship between the room-temperature and low-temperature structures may be discussed by regarding the latter as a configuration and orientation of the molecule in the unit cell at a potential energy minimum. The room-temperature structure can be derived from the low-temperature structure either by (i) static disorder of the unique low-temperature tetrahydroborate configuration among the three groups or (ii) dynamic exchange of configuration by each tetrahydroborate group. Gross disordering of molecules possessing the low-temperature structure which would require that boron atoms change places on cooling from room temperature to low temperature is considered to be unlikely since the requirements of fairly free rotation about the Al–N bond (to allow ordering at low temperature) and sharp potential minima (to account for comparatively localized boron sites even at room temperature) are incompatible.

(i) **Static Disordering of Tetrahydroborate Groups.**—In the room-temperature structure, each boron would be a "composite" peak composed of equal contributions from each boron atom configuration of the low-temperature structure. The separation of centers of the component boron atoms is 0.82 Å which is comparable with the value of 0.96 Å for the rms amplitude of thermal vibration of the composite boron atom perpendicular to the Al–B direction at room temperature. This static disordering seems unlikely since the separation of component atom centers (0.82 Å) is greater than the resolution limit of the X-ray data, but no splitting of peaks was observed.

(ii) **Dynamic Disordering of Tetrahydroborate Groups.**—If one invokes a dynamic exchange of configuration of the tetrahydroborate groups, the lack of resolution of the composite boron atoms would be explained. This dynamic mechanism would lead more easily to the substantially ordered low-temperature structure on cooling and might involve exchange of bridging and terminal hydrogen atoms.

Both of the above explanations would lead to substantial disorder of the hydrogen atoms of the tetrahydroborate groups at room temperature, and one would not expect to observe them on the room-temperature difference Fourier synthesis. Extensive rotation (or disordering) of the methyl groups at room temperature would make it unlikely that localized hydrogen atoms would be observed. However, at low temperature short contacts (of 1.93 Å) between hydrogen atoms on the methyl groups and bridging hydrogen atoms on the tetrahydroborate groups ($H_G(3)$ to $H_G(7)$ and the symmetry-related pair) would lock in the methyl groups with the ordered tetrahydroborate configuration. Table X lists all significant intramolecular and intermolecular contacts (together with esd's) based on the geometry of the low-temperature structure.

The present structure may be compared with the

Table IX

Atomic Vibration Ellipsoids at Room and Low Temperatures

		$\sqrt{\overline{u^2}}_{max}$, Å			$\sqrt{\overline{u^2}}_{med}$, Å			$\sqrt{\overline{u^2}}_{min}$, Å	
				(i) Room Temperature					
Al		0.345			0.302			0.286	
	0.000	0.000	1.000	0.281	−0.960	0.000	0.960	0.281	0.000
N		0.434			0.349			0.261	
	0.000	0.000	1.000	0.239	0.971	0.000	−0.971	0.239	0.000
C_S		0.553			0.427			0.276	
	0.000	0.000	1.000	0.166	−0.986	0.000	0.986	0.166	0.000
C_G		0.516			0.462			0.264	
	−0.377	−0.554	0.742	0.888	0.010	0.459	−0.262	0.832	0.489
B_S		0.511			0.488			0.285	
	0.000	0.000	1.000	0.032	−0.999	0.000	0.999	0.032	0.000
B_G		0.502			0.402			0.307	
	0.859	−0.458	−0.228	−0.434	−0.416	−0.799	0.271	0.786	−0.556
				(ii) Low Temperature					
Al		0.216			0.126			0.084	
	0.000	0.000	1.000	1.000	0.000	0.000	0.000	1.000	0.000
N		p.219			0.121			0.096	
	0.000	0.000	1.000	0.964	0.265	0.000	−0.265	0.964	0.000
C_S		0.273			0.180			0.131	
	0.000	0.000	1.000	0.307	0.952	0.000	−0.952	0.307	0.000
C_G		0.251			0.212			0.118	
	−0.093	−0.328	0.940	0.988	0.088	0.128	−0.125	0.940	0.316
B_S		0.306			0.177			0.117	
	0.000	0.000	1.000	0.746	0.666	0.000	−0.666	0.746	0.000
B_G		0.275			0.191			0.177	
	0.569	−0.266	−0.779	0.791	−0.082	0.606	−0.225	−0.961	0.164

Table X

Low-Temperature Intra- and Intermolecular Contacts (<2.5 Å)

Distance	Length, Å	Esd, Å
(i) Intramolecular		
N–H_G(3)	2.43	0.07
C_G–H_G(3)	2.34	0.07
C_G–H_G(9)′	2.42	0.10
H_S(1)–H_G(3)	2.39	0.10
H_S(1)–H_G(8)	2.35	0.11
H_G(2)–H_G(2)′	1.97	0.10
H_G(3)–H_G(7)	1.93	0.09
H_G(3)–H_G(8)	2.35	0.11
H_G(5)–H_G(7)	2.33	0.11
H_G(6)–H_G(7)	2.39	0.10
H_G(9)–H_G(9)′	1.87	0.14
(ii) Intermolecular		
H_S(1)–H_S(3) $(x - {}^1/_2, -{}^1/_2 - y, z)$	2.26	0.21
H_G(2)–H_G(9) $(x, 1 + y, z)$	2.45	0.13
H_G(4)–H_G(8) $(-x, -y, -z)$	2.48	0.12

trimethylarsine analog[11] which also crystallizes in space group Pnam with room-temperature unit cell parameters a = 14.60 Å, b = 7.16 Å, c = 11.66 Å, and Z = 4. The aluminum–arsenic bond is 2.55 Å; the coordination around the arsenic is approximately tetrahedral with a mean arsenic–carbon bond length of 1.98 Å. The coordination around the aluminum atom appears to resemble that of the low-temperature structure of the trimethylamine adduct with an angle to the special boron atom (As–Al–B_S) of 121°; the angle to the general boron atom (As–Al–B_G) is 93°. However, owing to the poor quality of the data, the positions of the boron atoms in this structure are not well determined (aluminum–boron distances are Al–B_S = 2.47 Å, Al–B_G = 2.18 Å) and no real significance can be attached to this apparent distortion from tetrahedral symmetry.

The present structures may also be compared with those of similar derivatives of alane, *i.e.*, $(CH_3)_3N\cdot AlH_3$ and $[(CH_3)_3N]_2AlH_3$. The former has been suggested[12] to have the aluminum tetrahedrally coordinated (from gas-phase infrared data), while the latter has been shown by X-ray analysis[13] to involve a monomeric trigonal-bipyramidal structure with an almost linear N–Al–N arrangement. The Al–N bond length (mean length 2.18 ± 0.01 Å) in $[(CH_3)_3N]_2AlH_3$ is considerably longer than that in $(CH_3)_3N\cdot Al(BH_4)_3$ (2.00 ± 0.01 Å), the latter being close to that expected from the sum of the covalent radii (1.96 Å), suggesting a relatively weaker bond in the alane derivative. Similarly long Al–N bond lengths (2.19 and 2.24 Å) are found in NNN′N′-tetramethylethylenediamine alane, which contains chains of AlH_3 units linked by the amine ligands with the aluminum again showing a trigonal-bipyramidal coordination.[14]

In the present structure, the tetrahedral configuration about the aluminum atom (for the $NAlB_3$ atoms) at room temperature is that expected for atoms of the group IIIb elements in simple 1:1 coordinate complexes. It further illustrates the change in hybridization which occurs about the aluminum atom on going from Al-

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$(BH_4)_3$, which is monomeric with a planar AlB_3 arrangement,[15] to the trimethylamine adduct. A similar tetrahedral symmetry around the aluminum atom has been observed in the adduct $C_6H_5C(Cl)O{\cdot}AlCl_3$,[16] the only other reported X-ray analysis on an $L{\cdot}AlX_3$ system (where L = ligand). It has been previously argued that the aluminum atom need use only one bonding orbital for each tetrahydroborate group,[17] and the mean positions of the boron atoms at room temperature suggest that the aluminum atom is essentially sp^3 hybridized. The distorted geometry around the aluminum atom at low temperature appears to represent a compromise with the boron and hydrogen atoms distorted from tetrahedral and pentagonal-bipyramidal sites, respectively, so that the planar geometry of each AlH_2B bridge system is preserved. The attempt by the boron atoms to occupy the tetrahedral sites may represent some degree of direct bonding between the aluminum and boron atoms; this is illustrated in Figure 3 in which the circles represent the normal (Sidgwick) covalent radii of atoms. Clearly the concept of coordination number must be used with care in any discussion of the stereochemistry of metal tetrahydroborates since the contribution of the bridge hydrogen atoms and boron atom may vary considerably depending on the size of the metal atom.

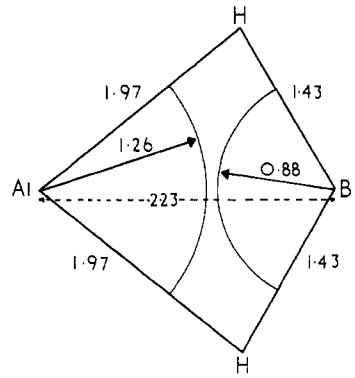

Figure 3.—Mean molecular geometry of AlH_2B system.

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A Variable-Temperature Proton Magnetic Resonance Study of Complexes of Pyridine, Methylpyridines, Ethylpyridines, Imidazole, 1-Methylimidazole, and Pyrimidine with Boron Trifluoride and Boron Trichloride

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A variable-temperature proton magnetic resonance chemical shift and coordination number study of complexes of pyridine, methylpyridines, ethylpyridines, imidazole, 1-methylimidazole, and pyrimidine with BF_3 and BCl_3 has been completed. In the presence of excess base, separate resonance signals are observed for bulk and complexed ligand molecules in all cases. The chemical shift data are interpreted in terms of paramagnetic shielding and polarization of the ligand molecules by complex formation. Integration of the bulk and complexed ligand signals for all systems shows conclusively that only one ligand molecule is complexed to BF_3 or BCl_3 from +35 to −40°. Mixed coordination number studies indicate a decreasing Lewis base strength in the order pyridine > 1-methylimidazole > imidazole and pyrimidine.

Introduction

Numerous nuclear magnetic resonance (nmr) studies of interactions of Lewis acids with a variety of ligands have been made in an attempt to assess the strength and structure of the complex formed. These investigations of the interactions of diamagnetic cations[1−3] and boron trihalides[4−12] with several Lewis bases are made by observing the chemical shifts of the ligand proton signals upon the addition of an equimolar amount of Lewis acid, usually in another solvent. The observed chemical shifts, however, reflect temperature and ionic strength effects, are influenced by interactions of the complexing species with solvent molecules, and frequently provide only qualitative information about the structure of the complex in solution.

It has been demonstrated recently that the spectra of solutions of various diamagnetic cations, such as

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